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<b>(54) Title:</b> WATER-ABSORBING COMPOSITIONS  <b>(57) Abstract</b>  A water-absorbent polymeric composition containing water-insoluble particles of a material which is substantially unreactive with the polymeric composition is disclosed. The water-insoluble particles are preferably particles of TiO <sub>2</sub> , clay or starch.		

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### Water-absorbing Compositions

The present invention relates to water-absorbing polymer compositions of the kind sometimes known as superabsorbent polymers. In particular, the present invention relates to water-absorbing polymers which include water-insoluble particles of a material which is substantially unreactive with the polymeric composition. Suitable additives include oxides of transition metals such as  $\text{TiO}_2$ , clay and starch.

Water-absorbing compositions are widely used in the manufacture of products which require high absorption capability; for example, surgical and dental sponges, tampons, sanitary napkins and pads, pant liners, adult incontinence pads, coverstock for feminine hygiene products, bandages, disposable diapers, patient underpads, mortuary pads, meat trays, wipes, domestic wipes, industrial wipes, packaging, filters, medical tray pads, fenestration drapes, other medical or surgical related articles, cable wrap, food preservation articles, seed germination pads, roofing materials, automotive trim, furniture, gasket sealants, pond liners, bedding, clothing, cement and household pet litter. Water-absorbing compositions are also used for the modification of soil to improve water retention and increase air capacity and for a host of other applications. It will be understood that some of the articles referred to are not per se absorbent but may be rendered absorbent by means of the presence in their structure, or at their surface of absorbent materials.

Water-absorbent compositions suitable for these and other uses may be in any suitable form including powders, fibers and filaments.

As used herein, the term "water" when used in the phrases "water-absorbing", "water-absorbent" and "water-swellaable" is understood to mean not only water but also aqueous media such as, in particular, electrolyte solutions such as body fluids.

A number of absorbent compositions have been developed which exhibit the capacity to be water-absorbing. For example, U.S. Patent numbers 3,954,721 and 3,983,095 disclose preparations for derivatives of copolymers of maleic anhydride with at least

one vinyl monomer in fibrous form. The fibrous copolymers are rendered hydrophilic and water-swellable by reaction with ammonia or an alkali metal hydroxide. U.S. Patent No. 3,810,468 discloses lightly cross-linked olefin-maleic anhydride copolymers prepared as substantially linear copolymers and then reacted with a diol or a diamine to introduce cross-linking. The resultant lightly cross-linked copolymers are treated with ammonia or an aqueous or alcohol solution of an alkali metal hydroxide. U.S. Patent No. 3,980,663 describes water-swellable absorbent articles made from carboxylic polyelectrolytes via cross-linking with glycerine diglycidyl ether. These patents are incorporated herein by reference.

European Published Application No. 0 268 498 (incorporated herein by reference) describes a water-absorbent composition formed by causing a substantially linear polymer of water-soluble ethylenically unsaturated monomer blends comprising carboxylic and hydroxylic monomers to cross-link internally.

Further examples of water-absorbent compositions are those produced from a copolymer of an  $\alpha,\beta$  unsaturated monomer having at least one pendant unit selected from a carboxylic acid group and derivatives thereof and a copolymerisable monomer. A proportion of the pendant units are present in the final copolymer as the free acid and a proportion as the salt of the acid. These copolymers are capable of being cross-linked, either internally or with a variety of cross-linking agents, to form the water-swellable composition. Examples of water-swellable compositions of this type can be found in U.S. Patent Nos 4,616,063, 4,705,773, 4,731,067, 4,743,244, 4,788,237, 4,813,945, 4,880,868 and 4,892,533 and European Patent Nos 0 272 074 and 0 264 208 and European Published Application No. 0 436 514 which are incorporated herein by reference.

Derivatives of carboxylic acid groups include carboxylic acid salt groups, carboxylic acid amide groups, carboxylic acid imide groups, carboxylic acid anhydride groups and carboxylic acid ester groups.

Other examples of water-absorbent compositions can be found in US 4798861,

WO93/17066, WO93/255735, WO93/24684, WO93/12275, European Published Application Nos 0 401 044, 0 269 393, 0 326 382, 0 227 305, 0 101 253, 0 213 799, 0 232 121, 0 342 919, 0 233 014, 0 268 498, and 0 397 410, British Patent Application Nos 2 082 614, 2 022 505, 2 270 030, 2 269 602 and 2 126 591, U.S. Patent Nos 4,418,163, 4,418,163, 3,989,586, 4,332,917, 4,338,417, 4,420,588 and 4,155,957 and French Patent Application No. 2 525 121 which are all incorporated herein by reference.

Whilst the water-absorbent compositions discussed above have a variety of uses, the physical properties of the resulting product may limit the applicability of the composition to a particular end use or its processability is restricted.

It has been discovered that by adding water-insoluble additives to the water-absorbent composition, the physical properties of the resulting composition may be enhanced.

In accordance with a first aspect of the present invention there is provided a water-absorbent polymeric composition containing water-insoluble particles of a material which is substantially unreactive with the polymeric composition.

The water-insoluble particles are preferably particles of  $\text{TiO}_2$ . The particles of  $\text{TiO}_2$  are preferably present in an amount of 0.1 to 25 wt %, more preferably 1 to 25 wt %.

The presence of the  $\text{TiO}_2$  in the water-absorbent polymeric composition may have a variety of effects. For example, the appearance of the composition is noted to have a shiny appearance when compared with compositions not including  $\text{TiO}_2$ . Further, a composition which is transparent in the absence of  $\text{TiO}_2$  may become opaque when  $\text{TiO}_2$  is added.

As with known water-absorbent compositions, compositions containing  $\text{TiO}_2$  may be in particulate, filament or fibrous form.

It has been found that  $\text{TiO}_2$  is compatible with the syrups from which superabsorbent

fibers are spun. In particular, the  $\text{TiO}_2$  is very compatible with a syrup comprising a copolymer of an  $\alpha,\beta$ -unsaturated monomer having at least one pendant unit selected from a carboxylic acid group and derivatives thereof and a copolymerisable monomer. A proportion of the pendant units are present in the final copolymer as the free acid and a proportion as the salt of the acid. These copolymers are capable of being cross-linked. The crosslinking may occur internally or external crosslinkers may be introduced. Suitable crosslinkers include compounds that will readily react with the pendant carboxylic acid groups of the copolymer such as alcohols and amines.

The  $\text{TiO}_2$  may be incorporated into this syrup in any suitable amount with amounts up to 25wt% being preferred, with amounts up to 15wt% being more preferred, and with an amount of from 0.2 to 11 wt% being particularly preferred. Thus, according to a second aspect of the present invention there is provided a crosslinkable composition comprising a (co)polymer have pendant carboxylic acid groups, or other groups convertible to carboxylic acid groups, wherein at least a portion of the carboxylic acid groups are partially neutralized, said composition containing  $\text{TiO}_2$ .

The presence of the  $\text{TiO}_2$  was found to facilitate the spinning of the syrup to form the fibers. Thus, according to a third aspect of the present invention there is provided the use of  $\text{TiO}_2$  in a crosslinkable polymeric syrup to improve the processability of the syrup into water-absorbent fibers.

Groups convertible to carboxylic acid groups include carboxylic acid salt groups, carboxylic acid amide groups, carboxylic acid imide groups, carboxylic acid anhydride groups and carboxylic acid ester groups.

The syrup preferably comprises a crosslinkable composition comprising a (co)polymer having pendant carboxylic acid groups, or other groups convertible to carboxylic acid groups, wherein at least a portion of the carboxylic acid groups are partially neutralized. The syrup preferably additionally comprises a composition capable of crosslinking the (co)polymer.

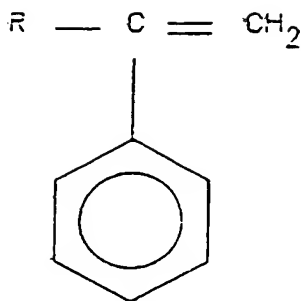
Fibers formed from a syrup including  $\text{TiO}_2$  were found to have a better appearance and softness than those produced in the absence of  $\text{TiO}_2$ . Further, the presence of the additive was found not to have a deleterious effect on the absorbency of the resultant fibers and in some cases was found to improve the absorbency.

5 Particularly suitable copolymers for use in the production of the water-absorbing compositions used in the present invention will contain from about 25 to about 75 mole percent recurring units of at least one  $\alpha,\beta$ -unsaturated monomer and from about 75 to about 25 mole percent recurring units of at least one copolymerizable monomer. The copolymer preferably contains from about 35 to about 65 mole percent of  
10 recurring units of at least one  $\alpha,\beta$ -unsaturated monomer and from about 65 to about 35 mole percent of at least one copolymerizable co-monomer. Most preferably, the copolymer will be an equimolar copolymer.

Suitable  $\alpha,\beta$ -unsaturated monomers are those bearing at least one pendant carboxylic acid unit or derivative of a carboxylic acid unit. Derivatives of carboxylic acid units  
15 include carboxylic acid salt groups, carboxylic acid amide groups, carboxylic acid imide groups, carboxylic acid anhydride groups and carboxylic acid ester groups.

Examples of suitable  $\alpha,\beta$ -unsaturated monomers include maleic acid, crotonic acid, fumaric acid, mesaconic acid, the sodium salt of maleic acid, the sodium salt of 2-methyl, 2-butene dicarboxylic acid, the sodium salt of itaconic acid, maleamic acid,  
20 maleamide, N-phenyl maleimide, maleimide, maleic anhydride, fumaric anhydride; itaconic anhydride, citraconic anhydride; mesaconic anhydride, methyl itaconic anhydride, ethyl maleic anhydride, diethylmaleate, methylmaleate; and the like, and their mixtures. Monomers having two carboxylic acid groups attached to adjacent carbon atoms are particularly preferred.

25 Any suitable copolymerizable co-monomer can be employed. Examples of suitable copolymerizable co-monomers include ethylene, propylene, isobutylene,  $\text{C}_1$  to  $\text{C}_4$  alkyl acrylates,  $\text{C}_1$  to  $\text{C}_4$  alkyl methacrylates, vinyl acetate, vinyl alcohol, methyl vinyl ether, isobutyl vinyl ether, and styrenic compounds having the formula:



wherein R represents hydrogen or an alkyl group having from 1 to 6 carbon atoms, and wherein the benzene ring may be substituted with low molecular weight alkyl or hydroxyl groups.

5 Sutable  $\text{C}_1$  to  $\text{C}_4$  alkyl acrylates include, for example, methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, and the like, and their mixtures.

Sutable  $\text{C}_1$  to  $\text{C}_4$  alkyl methacrylates include, for example, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propylmethacrylate, n-butyl methacrylate, and the like, and their mixtures.

10 Sutable styrenic compounds include, for example, styrene,  $\alpha$ -methylstyrene, p-methylstyrene, t-butylstyrene, and the like, and their mixtures.

The copolymerizable comonomer may provide groups that can react with the carboxylic acid group to cross link the polymer. Sutable groups include hydroxy groups and amine groups.

15 The pendant units on the  $\alpha,\beta$ -unsaturated monomer, will determine what, if any, additional reactions must be carried out to obtain a copolymer having the requisite pendant units necessary to produce the water-absorbing compositions of this invention. Preferably these water-absorbing compositions will contain from about 20 to about 80 percent pendant carboxylic acid units and from about 80 to about 20  
20 percent pendant carboxylate salt units. Preferably, both units are present in an amount of from about 30 to about 70 percent.



In general, if the  $\alpha,\beta$ -unsaturated monomer bears only carboxylic acid amide, carboxylic acid imide, carboxylic acid anhydride, carboxylic acid ester groups or mixtures thereof, it will be necessary to convert at least a portion of such carboxylic acid derivative groups to carboxylic acid groups by, for example, a hydrolysis reaction. If the  $\alpha,\beta$ -unsaturated monomer bears only carboxylic acid salt groups, acidification to form carboxylic acid groups will be necessary using methods and materials well known in the art.

Similarly, the final copolymer should contain from about 80 to 20 percent pendant carboxylate salt units. Accordingly, it may be necessary to carry out a neutralization reaction. Neutralization of carboxylic acid groups with a strong organic or inorganic base such as NaOH, KOH, ammonia, ammonia-in-water solution, or organic amines will result in the formation of carboxylate salt units, preferably carboxylate metal salt units.

The sequence and the number of reactions (hydrolysis, acidification, neutralization, etc.) carried out to obtain the desired functionality attached to the copolymer backbone are not critical.

One copolymer particularly suitable for use in the present invention is a copolymer of maleic anhydride and isobutylene. Another is maleic anhydride and styrene. Suitable copolymers will have peak average molecular weights of from about 6,000 to about 500,000 or more.

Suitable copolymers of maleic anhydride and isobutylene can be prepared using any suitable conventional method. Such copolymers are also commercially available from Kurary Isoprene Chemical Company, Ltd., Tokyo, Japan. under the trademark ISOBAM. ISOBAM copolymers are available in several grades which are differentiated by average viscosity molecular weight: ISOBAM-10, 160,000 to 170,000; ISOBAM-06, 80,000 to 90,000; ISOBAM-04, 55,000 to 65,000, and ISOBAM-600, 6,000 to 10,000.

The copolymer is then preferably cross-linked either internally or using an external cross-linking agent. Suitable cross-linking agents include: monomers containing at least two hydroxyl groups such as alkylene glycols containing 2-10 carbon atoms and their ethers, cycloalkylene glycols, Bisphenol A, hydroxy alkylene derivatives of Bisphenol A, hydroquinone, phloroglucinol, hydroxy alkylene derivatives of diphenols, glycerol, erythritol, pentaerythritol, and mono-, di or oligo-saccharides; heterocyclic carbonates; and monomers containing at least one amine group and at least one hydroxyl group such as ethanolamine, tris (hydroxymethyl) aminomethane, 3-amino-1-propanol, DL-1-amino-2-propanol, 2-amino-1-butanol, N,N-dimethylethanolamine, diisopropanol-amine methyl diethanol amine, triethanol amine, 2-(methylamino)ethanol and the like.

In general cross-linking will not occur and the product will not become absorbent until the partially neutralized polymer reaction product is heated to a temperature sufficient to effect reaction between the cross-linking agent and the copolymer.

The cure conditions required to achieve optimal cross-linking depends upon several factors, including the particular polymer employed. For example, the cure temperature will depend on the polymer. If the polymer is a partially neutralized ethylene/maleic anhydride copolymer, a cure temperature of at least 140°C will be required to achieve cross-linking. If the polymer is partially neutralized styrene/maleic anhydride copolymer, a temperature of at least about 150° is required to cross-link; and if a partially neutralized isobutylene/maleic anhydride copolymer is employed, a temperature of at least about 170°C will be required to achieve cross-linking. Cure times can vary depending on cure temperature and on the amount of reactive compound used. Cure times will typically be within the range of from about 0.5 to about 20 minutes, preferably 0.5 to 15 minutes, and most preferably 0.5 to 12 minutes. To maximize absorbent properties, optimal cure of the composition (i.e. minimal amount of cross-linking needed to form a cross-linked network) is required. Optimal cure is achieved by adjusting a number of variables within wide ranges depending upon the specific syrup composition. Optimal cure conditions require, among other things, a balance between cure time and cure temperature.

As is readily apparent from the high temperature required to achieve cross-linking, the aqueous reaction product of the partially neutralized polymer and the reactive compound, i.e. the grafted polymer syrup, can be stored for an unlimited time. This unlimited room temperature stability facilitates further processing of the syrup into any number of conventional forms, including fibers and films using conventional methods. For example, the syrup can be further processed by casting, spray drying, air-assisted spray drying, air attenuation, wet spinning, dry spinning, flash spinning, and the like. To facilitate the removal of water from the aqueous composition during the spinning process, minor amounts of other polar solvents such as alcohol can be added to the aqueous syrups. The resultant fibers can be further processed into milled fibers, chopped fibers, fluff or bulk fibers, strands, yarns, webs, composites, woven fabrics, non-woven fabrics, non-woven mats, tapes, scrim, and the like, using a variety of methods including twisting, beaming, slashing, warping, quilling, severing, crimping, texturizing, weaving, knitting, braiding, etc., and the like. In addition, the syrup may be used to coat yarns, articles or individual fibers. The coating may be discontinuous. This is to say the coating may be applied as spaced nodules.

The water-absorbent compositions may be formed into a composite web comprising non-water absorbent fibers and water-absorbent fibers. The fibers of these webs may be bonded using any suitable technique. Suitable non-water-absorbent fibers include rayon fiber, cellulose ester fiber, protein fiber, viscose fiber, polyamide fiber, polyester fiber, polyvinyl fiber, polyolefin fiber, polyurethane fiber, aramid fiber, fibers formed from non-water-absorbent polymers of ethylene, non-water-absorbent polymers of propylene, polyamide and ethylene-propylene copolymer fibers, and glass fibers and mixtures thereof. The non-water-absorbent fibers having hollow cores such as the polyester, typically polyethylene terephthalate fibers commercially available from E.I. DuPont de Nemours under the trade mark HOLLOWFILL are also suitable.

The present invention as it relates to the water-insoluble particles being particles of  $\text{TiO}_2$  will now be described with reference to the following examples.

The samples produced in the examples which follow were tested to determine their

absorbent properties using conventional test procedures to measure the unit of liquid (saline) absorbed per unit of fiber sample (Free Swell Index) and the unit of liquid (saline) retained per unit of fiber sample after subjecting the swelled fiber sample to 0.5 psi.

- 5 The Free Swell Index test procedure used is described in U.S. Pat No. 4454055, the teachings of which are incorporated herein by reference. To determine the Free Swell Index at atmospheric (room) pressure, about 0.2 to 0.3g of about 3/4 in. cured water-absorbing fibers to be tested were placed in an empty W-shaped tea bag. The tea bag containing the fibers was immersed in brine (0.9 wt% NaCl) for 10 minutes, removed and allowed to sit on a paper towel for 30 seconds to remove surface brine. The Free Swell Index of the fiber, that is the units of liquid absorbed per each unit of sample, is calculated using the following formula:

$$\text{Swell Index} = \frac{\text{Weight of Wet Fibers}}{\text{Weight of dry Fibers}} \quad -1$$

- 15 To determine Free Swell Index under pressure (0.5 psi retention), the following modified procedure was used.

After the tea bag containing the fiber sample was immersed in brine and surface brine had been removed, it was immediately placed in a 16 cm ID Buchner funnel fitted with a 2000 ml sidearm vacuum filter flask and connected to a manometer. A piece of dental dam rubber sheeting was securely fixed over the mouth of the funnel such that the sheeting just rested on the tea bag. Next, a vacuum sufficient to create the desired pressure was drawn on the flask for a period of 5 minutes, and the Free Swell Index under pressure was calculated using the above formula.

#### Example 1

- 25 Water-absorbent fibers having a thickness of 2 - 3 denier and containing 0, 0.2, 11 or 15 wt% TiO<sub>2</sub> were produced. The absorption capacity of these fibers was measured using 0.9% saline and the results obtained are set out in Table 1.

Table 1

Amount of TiO <sub>2</sub>	0 wt% TiO <sub>2</sub>	0.2 wt%TiO <sub>2</sub>	11 wt%TiO <sub>2</sub>	15 wt%TiO <sub>2</sub>
Free Swell (g/g)	47	52	50	47
0.5 PSI Retention (g/g)	28	31	31	28

**Example 2**

The absorption for the fibers containing 0.2wt% TiO<sub>2</sub> was measured using sheeps' blood and compared with that for fibers that were free of TiO<sub>2</sub>. The results are set out in Table 2.

Table 2

Amount of TiO <sub>2</sub>	0 wt% TiO <sub>2</sub>	0.2 wt% TiO <sub>2</sub>
Free Swell (g/g)	9.3	27.1

Thus, the fibers containing TiO<sub>2</sub> were found to have improved absorption capacity and retention over the fibers alone.

Further, when fibers, filaments or powders formed from a water-absorbent polymeric composition containing TiO<sub>2</sub> are formed into a composite pad they are found to exhibit excellent rewet properties. Rewet is a measure of how dry the fibers, filaments or powder feel to the touch after water-absorption. This is a particularly important in applications such as sanitary towels and diapers where if the fibers, filaments or powder feel damp the user will feel damp and uncomfortable.

Rewet is measured by forming the polymeric composition in fibrous, filament or powder form into a 3" composite pad. 15mls of 0.9% saline solution is added to the composite pad at a rate of 2ml/sec. After 15 minutes, 10 preweighed Whatman <sup>TM</sup> #3

filter papers (dry weight W1) are placed on top of the composite pad and a 3Kpa load is applied for 2 minutes. The filter papers are then removed and reweighed (wet weight W2). Rewet can then be calculated according to the following formula:

$$\text{Rewet} = W1 - W2.$$

### Example 3

Pads of non-water-absorbent fibers and fibers of the present invention were produced and their absorbency was measured using the dunk test and the inclined wicking test. In the dunk test the pad was immersed in saline for 5 minutes, the pads are then weighed and the amount of saline absorbed is calculated. In the inclined wicking test a 10cm x 10 cm sample is located with one end of the pad in the saline and the pad supported such that it is inclined at 30° to the bench. The distance of travel of the liquid front is measured after 20 minutes. The compositions of the samples and the results of the tests are set out in Table 3.

Table 3

Sample No	Amount of TiO <sub>2</sub> (%)	Basis Weight (gsm)	Super-absorbent fiber %	Density	Dunk (g)	Inclined Distance (g)
3-1	0.3	94	15	0.13	13.5	12
3-2	0.3	152	15	0.14	17	14
3-3	0.3	173	15	0.14	15	17
3-4	0.3	193	15	0.16	14	15
3-5	0.3	256	25	0.17	17	14

It will be understood that the absorbency of the fiber is not adversely effected by the presence of the TiO<sub>2</sub>.

Other water-insoluble particles which may be contained in the water-absorbent

polymeric composition include clay and starch, preferably corn starch. Particles of clay or starch are preferably added as fillers and therefore result in an economic saving in the production of the polymeric composition.

Other benefits are derived from the presence of particles of clay or starch in the polymeric composition. These benefits include lower % extractables and improved gel strength. Further, there is little or no deleterious affect on other properties such as absorption and wicking.

If fibers are to be formed of the water-absorbent composition, the clay or starch are preferably added directly to the aqueous syrup from which fibers will be spun. Both clay and starch are compatible with the syrup and do not interfere with the spinning process.

The clay or starch may be added in an amount of up to 25 wt%. It will be understood that the discussion of suitable copolymers given above in relation to the particles being  $\text{TiO}_2$ , applies equally to the embodiment of the invention where the particles are clay or starch.

The present invention as it relates to the water-insoluble particles being particles of clay or starch will now be described with reference to the following examples.

#### Example 4

Water-absorbent fibers 50% neutralized Isobam <sup>TM</sup> (copolymer of isobutylene and maleic anhydride available from Kuraray Isoprene Chemical Company Ltd., Tokyo, Japan), propylene carbonate and clay: Bentonite SD-2 is a composition containing 13% Bentonite powder based on Isobam weight. The properties of these fibers were then compared with fibers formed in the absence of clay. The results are set out in Table 4.

Table 4

Property	0% Bentonite	13% Bentonite SD-2
Free Swell (g/g)	32.9	36.8
0.5psi retention (g/g)	24.7	22.2
% Solubility	13.7	10.2
Gel strength	Good	Excellent

**Example 5**

Example 4 was repeated with the clay being replaced by 2% and 25% corn starch. The results are set out in Table 5.

Table 5

Property	0% Corn Starch	2% Corn Starch	25% Corn Starch
Free Swell (g/g)	40	40	41
0.5psi retention (g/g)	27.8	28.4	27.6
% Solubility	14.7	10.6	9.2

The water-absorbing polymer compositions of the present invention may be used in the manufacture of a variety of products which require a high absorption capability. Thus according to a further aspect of the present invention there is provided an article of manufacture comprising the water-absorbent polymeric composition of the above first aspect.



## CLAIMS

1. A water-absorbent polymeric composition containing water-insoluble particles of a material which is substantially unreactive with the polymeric composition.
2. A water-absorbent polymeric composition according to Claim 1, wherein the water-insoluble particles are particles of  $\text{TiO}_2$ .
3. A water-absorbent polymeric composition according to Claim 2, wherein the particles of  $\text{TiO}_2$  are present in an amount of 0.1 to 25 wt%, preferably 1 to 25 wt %.
4. A water-absorbent polymeric composition according to Claim 1, wherein the polymeric composition is in particulate, filament or fibrous form.
5. A crosslinkable composition comprising a (co)polymer having pendant carboxylic acid groups or other groups convertible to carboxylic acid groups, wherein at least a portion of the carboxylic acid groups are partially neutralized, said composition containing  $\text{TiO}_2$ .
6. A crosslinkable composition according to Claim 5 wherein the  $\text{TiO}_2$  is present in an amount of 0.1 to 25 wt%, preferably 1 to 25 wt %.
7. A crosslinkable composition comprising to Claim 5 additionally comprising a composition capable of crosslinking the (co)polymer.
8. The use of  $\text{TiO}_2$  in a crosslinkable polymeric syrup to improve the processability of the syrup into water-absorbent fibers.
9. The use according to Claim 8 wherein the syrup comprises a crosslinkable composition comprising a (co)polymer having pendant carboxylic acid groups or other groups convertible to carboxylic acid groups, wherein at least a portion of the carboxylic acid groups are partially neutralized.

10. The use according to Claim 9 wherein the syrup additionally comprises a composition capable of crosslinking the (co)polymer.
11. The use of  $\text{TiO}_2$  in a water-absorbent polymeric composition.
12. A water-absorbent polymeric composition according to Claim 1 wherein the water-insoluble particles are particles of clay.
13. A water-absorbent polymeric composition according to Claim 12 wherein the clay particles are present in an amount of up to 25wt%.
14. A water-absorbent polymeric composition according to Claim 1, wherein the water-insoluble particles are particles of starch.
15. A water-absorbent polymeric composition according to Claim 14, wherein the starch particles are present in an amount of up to 25wt%.
16. An article of manufacture comprising the water-absorbent polymeric composition of Claim 1.

## INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 96/01262

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C08K11/00 D01F6/36 A61L15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 441 975 (NIPPON CATALYTIC CHEM IND) 21 August 1991 see claims 1-31 ---	1-3,5, 11,16
X	US,A,4 587 308 (MAKITA MUNE HARU ET AL) 6 May 1986 see example 10; table 1 see claims 1-10 ---	1-3,5,6
X	DATABASE WPI Derwent Publications Ltd., London, GB; AN 94-276180 XP002008931 & JP,A,06 207 400 (HIROSE SEISHI KK, WASHINO ISHIKAWA KK) , 26 July 1994 see abstract -----	1-3

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

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- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
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Date of the actual completion of the international search

19 July 1996

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 96/01262

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